Occurrence of TBA in Ground Water

A Summary of Existing Studies

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Outline

- Potential Dissolution From Gasoline?
- Potential In-situ Biodegradation of MTBE?
- Potential Abiotic Transformation of MTBE?
  - Artifacts of sampling and analytical protocols
  - In-situ transformation?

- Potential Biodegradation of TBA

Potential Dissolution From Gasoline

Gasoline-Water Equilibrium Partitioning

$$C_{TBA}^{water} = C_{MTBE}^{water} * \left(\frac{TBA}{MTBE} \right)_{gasoline} * \left(\frac{K_{fw}^{MTBE} + \frac{V_{wat}}{V_{gas}}}{K_{fw}^{TBA} + \frac{V_{wat}}{V_{gas}}} \right)$$

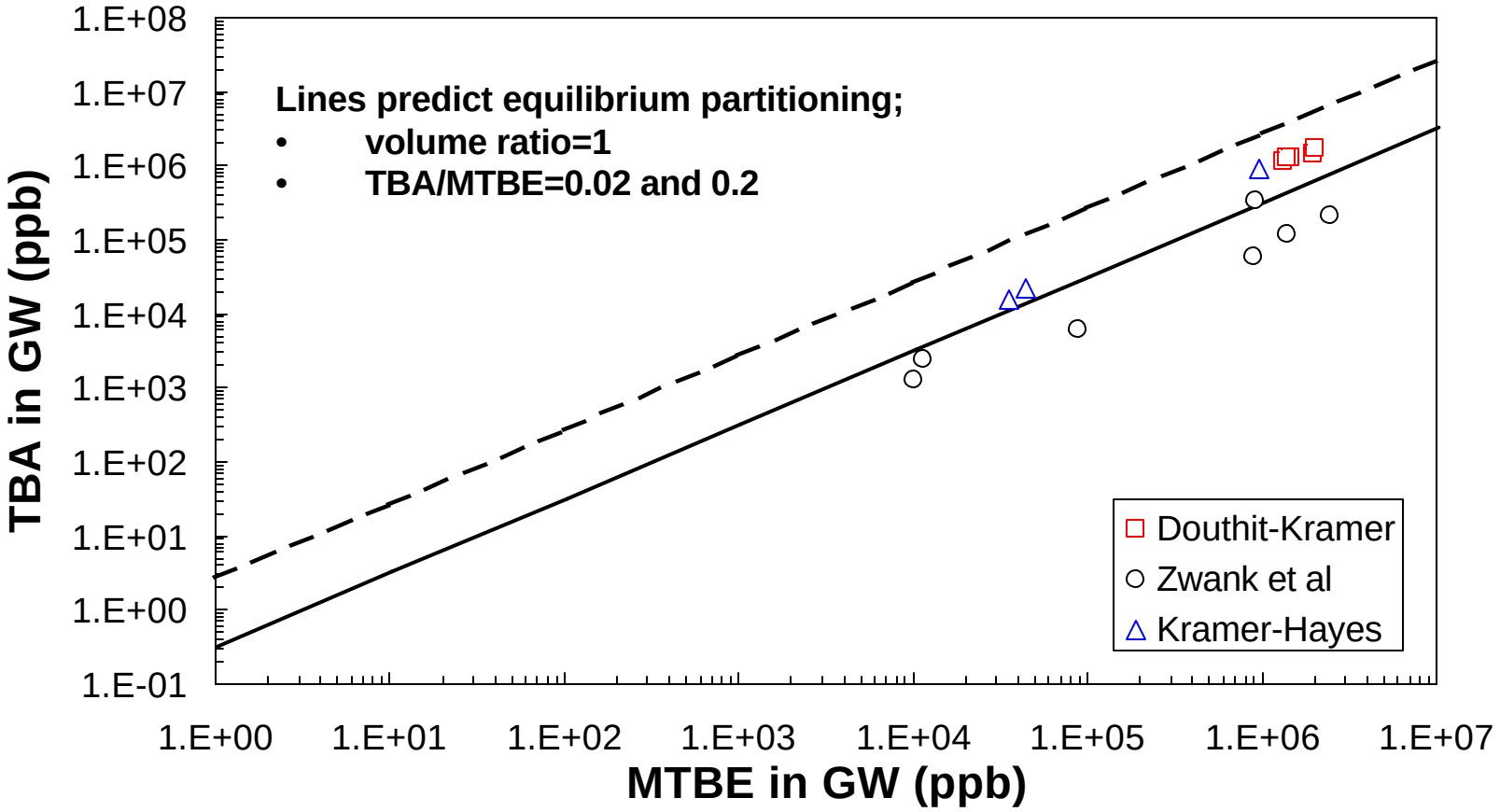
- Where, K_{fw} are fuel-water partitioning coefficients (mg/L in fuel/mg/L in water at equilibrium)
  - K_{fw}^{MTBE} = 15.5 (Cline et al., 1991)
  - K_{fw}^{TBA} = 0.24, average of 0.15 and 0.33 (Zwank et al., 2002)
- Kramer-Douthit, 2000. (volume ratio = 4)
- Zwank and others, 2002. (volume ratio = 1)
- Kramer and Hayes, 1987. (volume ratio =1)

Estimated TBA and MTBE Content in Gasoline – Analyses of Past Studies

Measured MTBE (aq) (ppb)	Measured TBA (aq) (ppb)	Estimated TBA/MTBE in original gasoline %w/w	Estimated TBA/MTBE in original gasoline %v/v	Estimated %v/v in gasoline MTBE	Estimated %v/v in gasoline TBA
Kramer-Douthit Data (2000 expts)					
1330000	1120000	**18.3%**	**17.2%**	3.5%	0.6%
1990000	1430000	**15.6%**	**14.7%**	5.2%	0.8%
1480000	1270000	**18.7%**	**17.5%**	3.9%	0.7%
2000000	1690000	**18.4%**	**17.2%**	5.3%	1.0%
1390000	1270000	**19.9%**	**18.6%**	3.7%	0.7%
Zwank et al. 2002 data (persoanl communication with Dr. Schmidt)					
917638.4	341462.4	**2.80%**	**2.62%**	2.046%	0.057%
11523.2	2415.1	**1.58%**	**1.48%**	0.026%	0.000%
10187.5	1318.0	**0.97%**	**0.91%**	0.023%	0.000%
1397587.6	121435.5	**0.65%**	**0.61%**	3.116%	0.020%
2455632.0	212639.4	**0.65%**	**0.61%**	5.475%	0.036%
87723.4	6067.4	**0.52%**	**0.49%**	0.196%	0.001%
888152.2	59060.4	**0.50%**	**0.47%**	1.980%	0.010%
Kramer and Hayes (1987)					
43700	22300	**3.83%**	**3.60%**	0.097%	0.004%
35100	15900	**3.40%**	**3.19%**	0.078%	0.003%
966000	933000	**7.26%**	**6.81%**	2.154%	0.156%

TBA in GW – Potential Sources

Analyses of Past Studies



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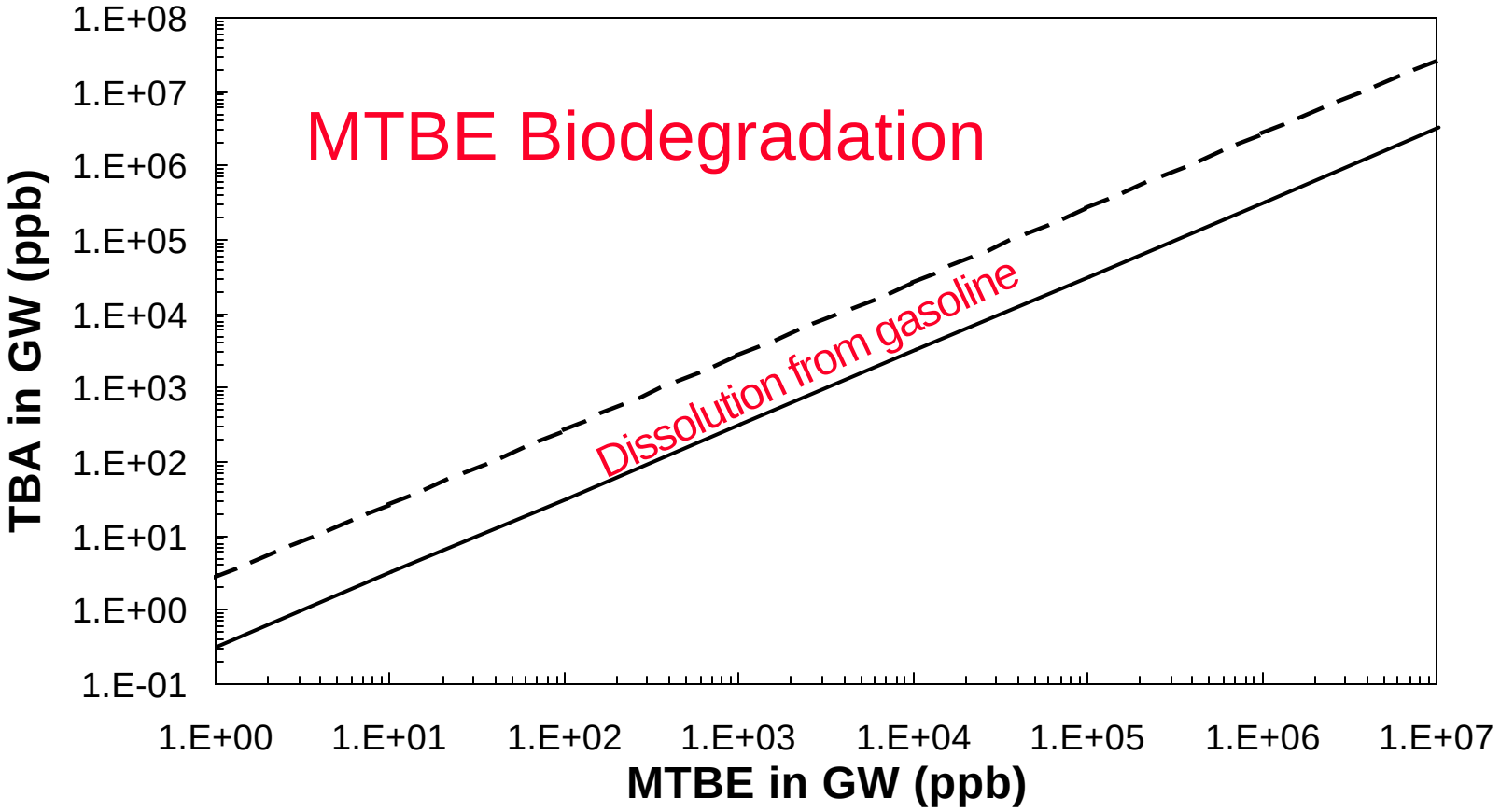
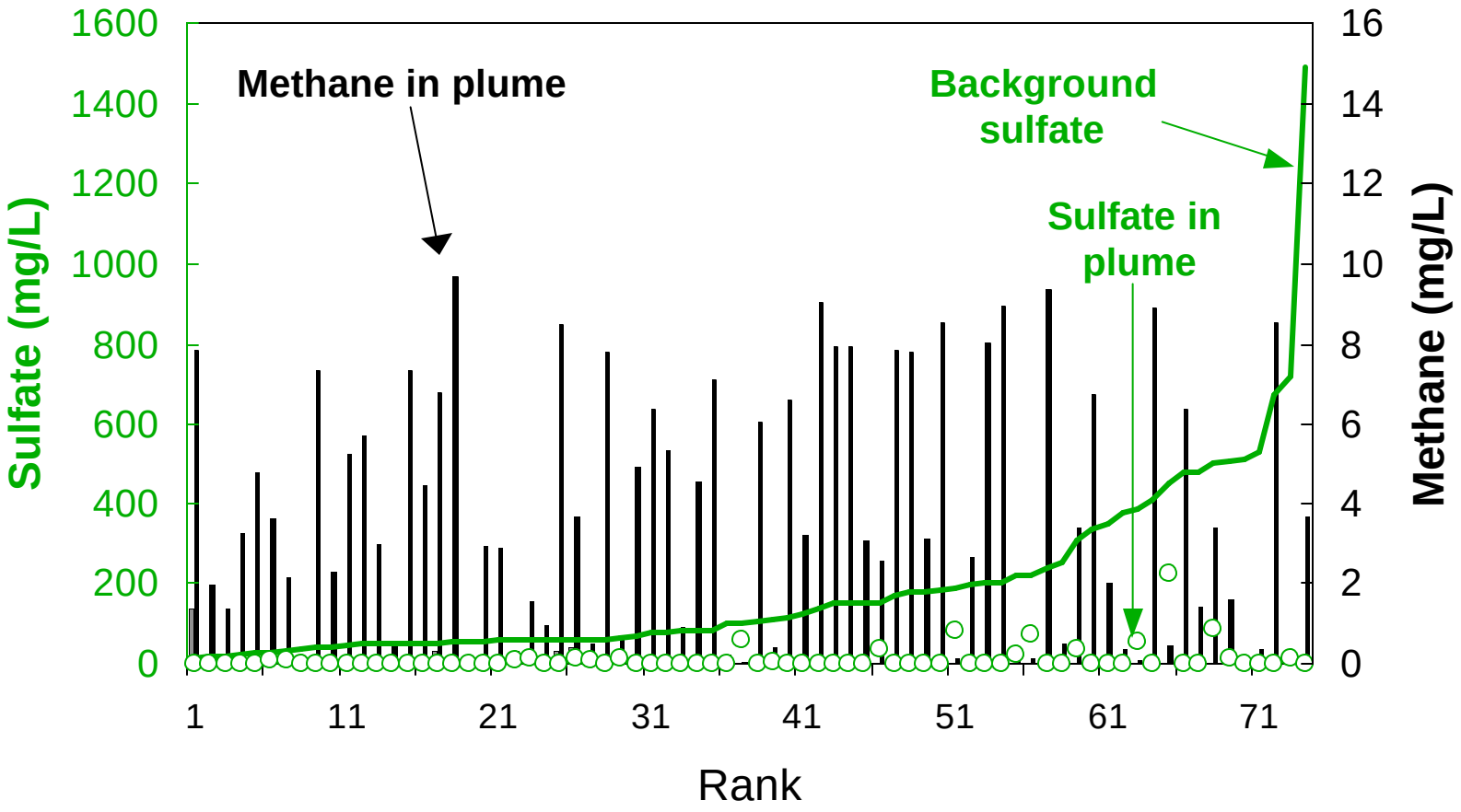


Potential MTBE Biodegradation

Scope of BP-EPA Study

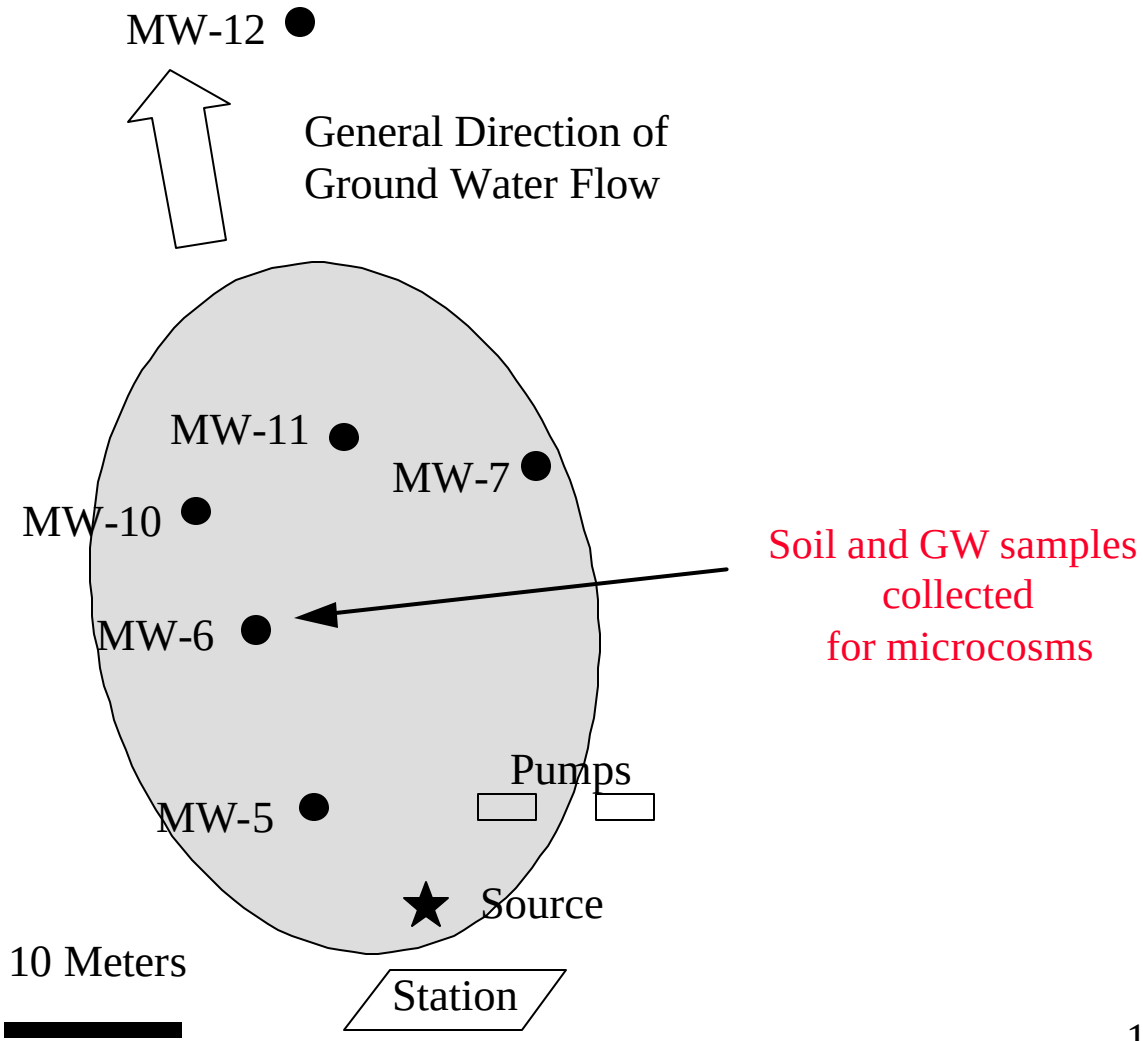
- 7 States + Washington DC
- 700 ground water samples from 74 BP retail sites in 50 cities (1999)
- Another 250 ground water samples from 18 sites (2000)
- **GW samples preserved with Tri-sodium Phosphate (TSP)**

Ground Water Geochemistry
BP-EPA Study

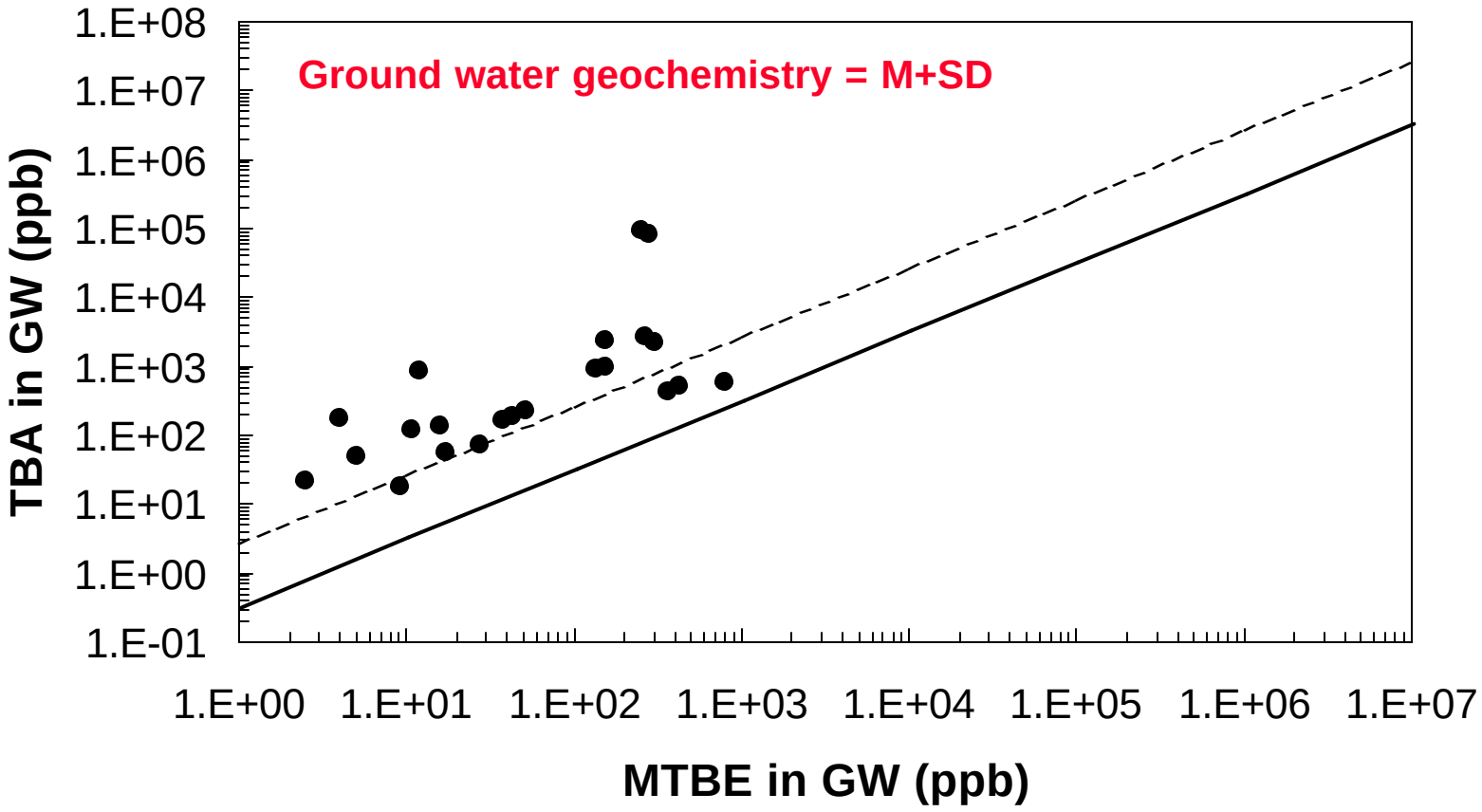


Majority of plumes are methanogenic-sulfate depleted

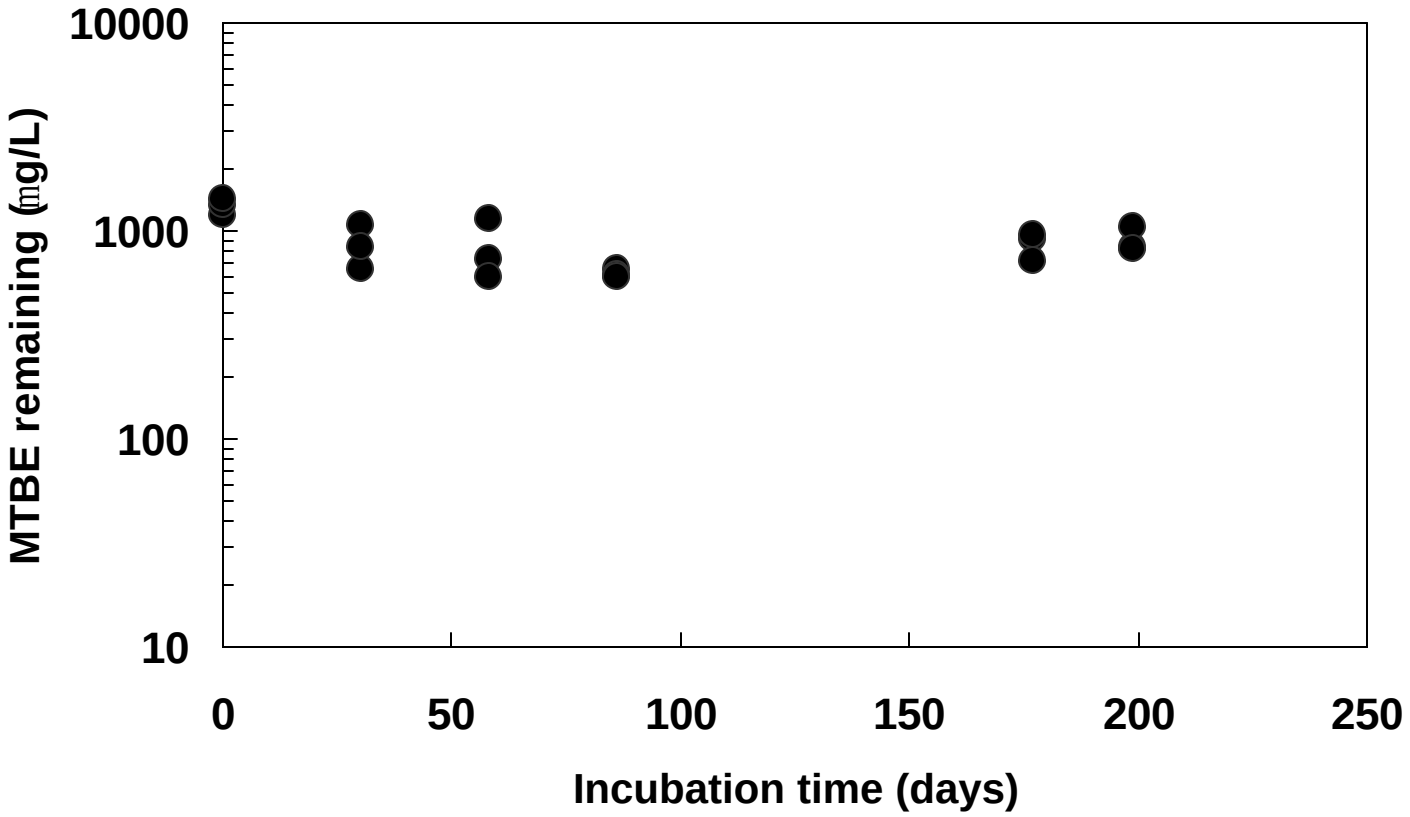
Site in NJ
BP-EPA Study



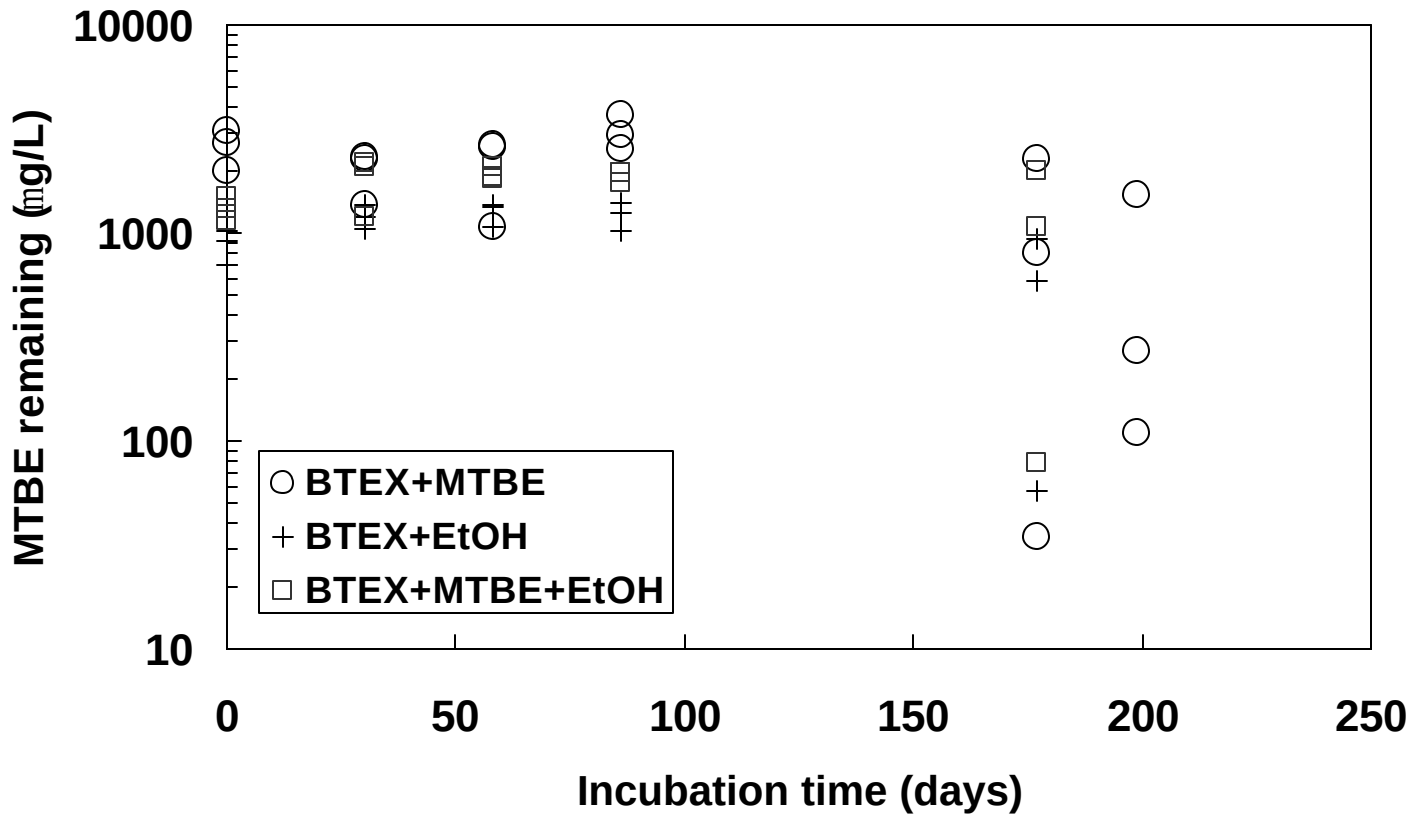
TBA in GW at NJ Site
BP-EPA Study



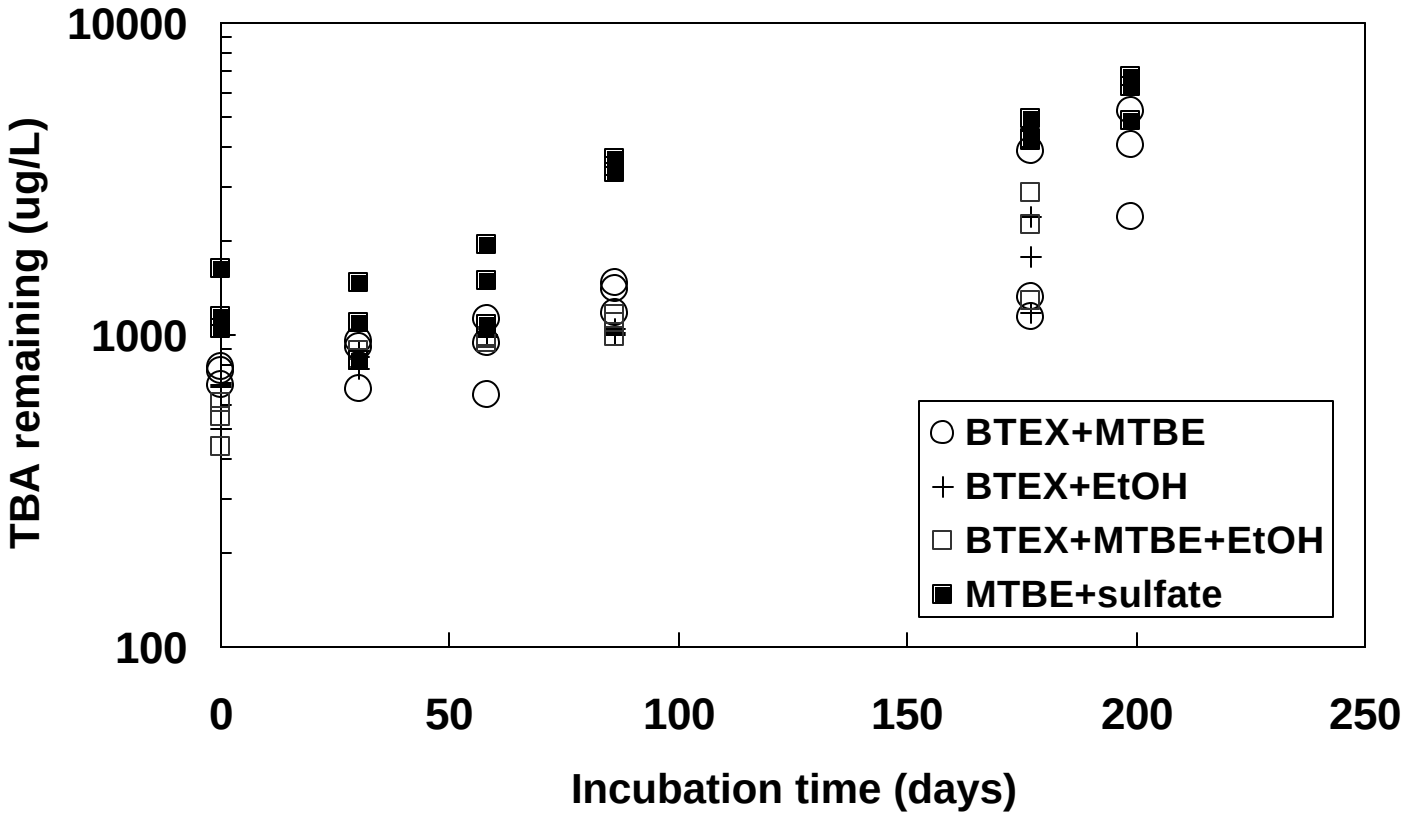
Laboratory Microcosms - Killed Controls BP-EPA Study



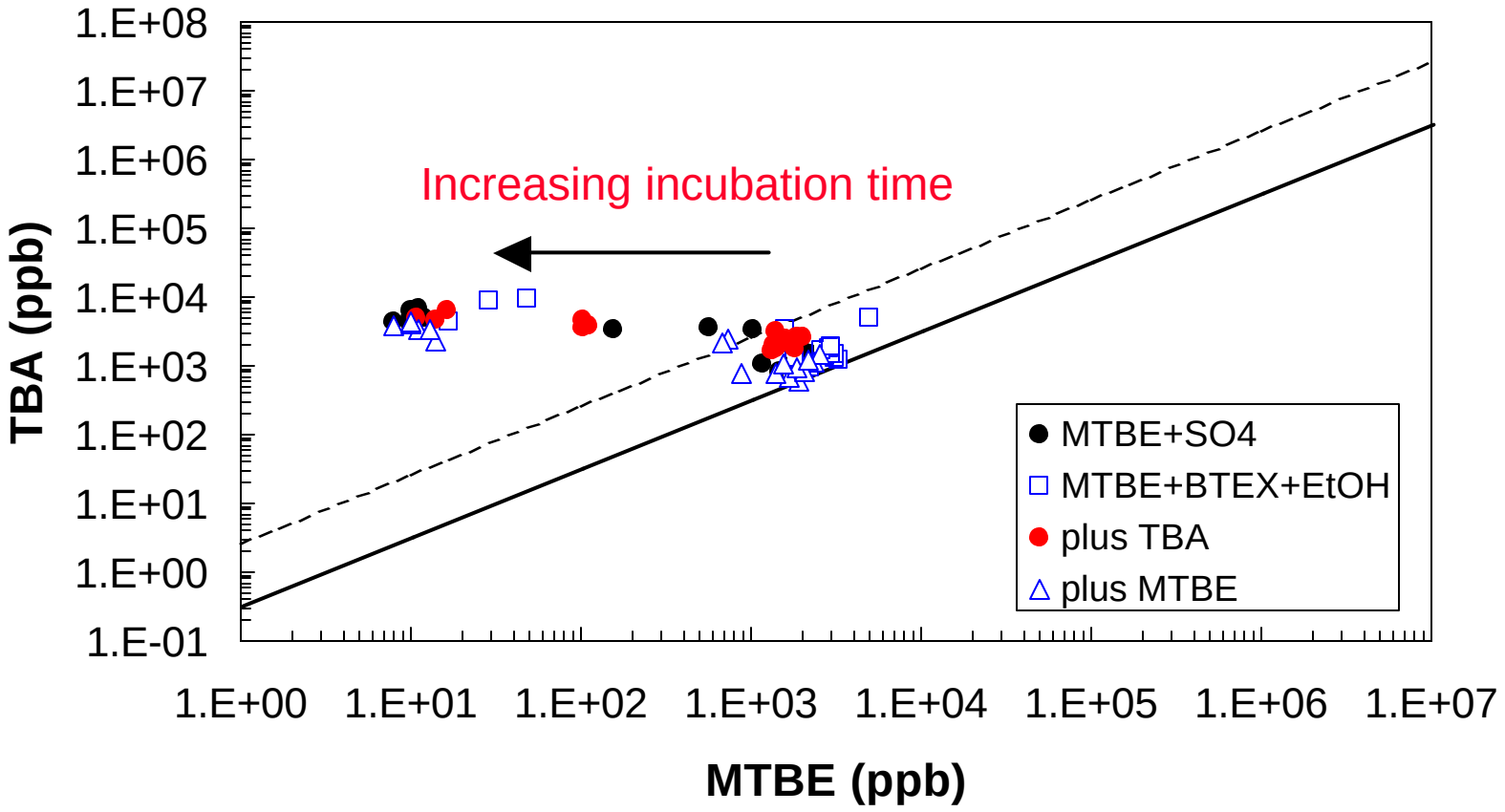
Laboratory Microcosms Indicating MTBE Biodegradation BP-EPA Study



TBA in Live Laboratory Microcosms BP-EPA Study



TBA in Anaerobic Microcosms (NJ Site) BP-EPA Study



This is consistent with USGS' observation

Potential Abiotic Transformation

Potential Sample Preservation and Shipping Issues

- Potential for Acid Hydrolysis of MTBE in HCl-preserved ground water samples (O'Reilly et al. 2001)
- Hydrolysis Rate Constant (personal communication with Dr. John Wilson, EPA)

$$\ln k_{pH=2} = \frac{-14360}{(273+t)} + 38.699 \text{ at } pH = 2$$

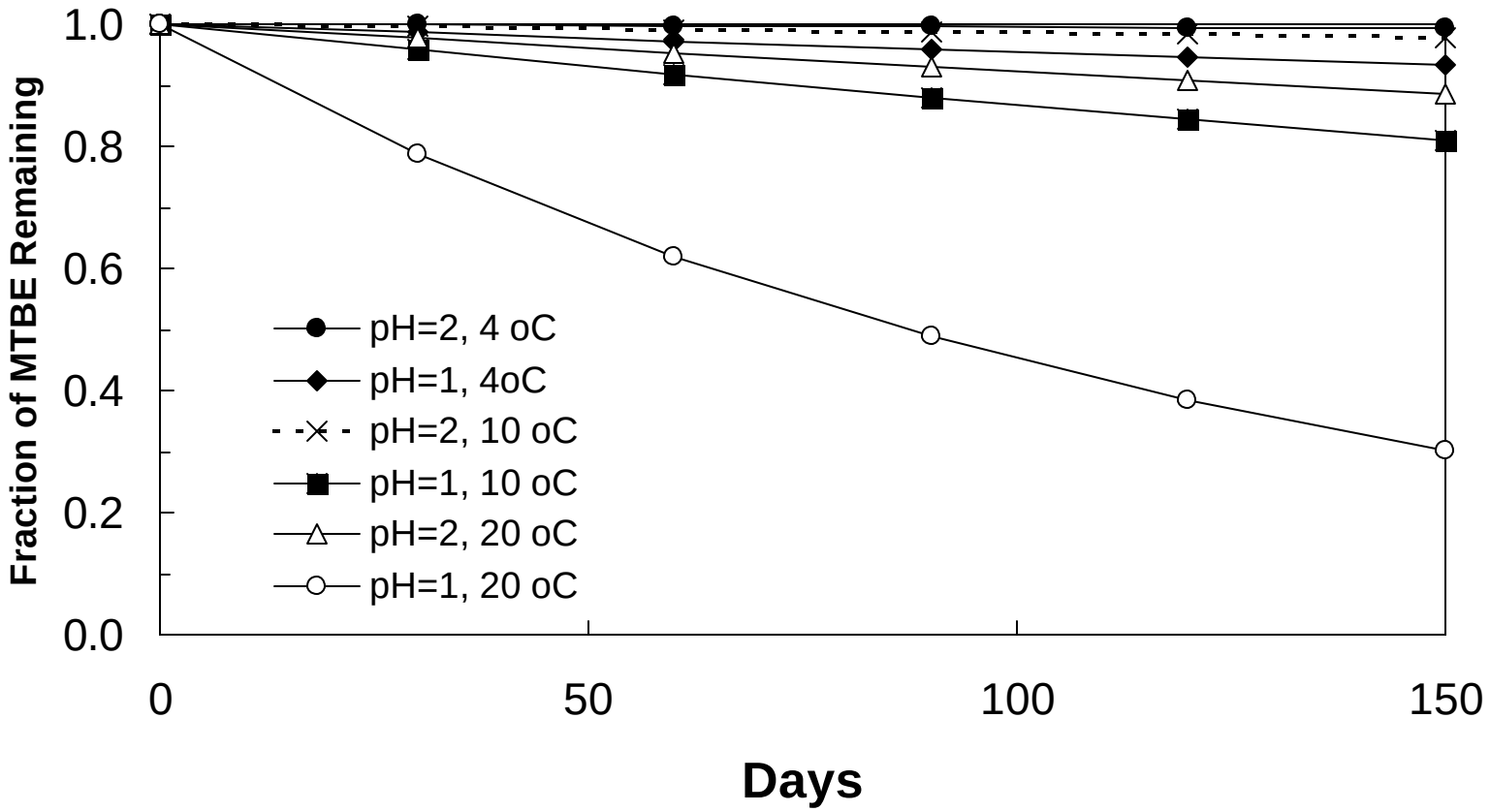
where,

$k_{pH=2}$ = rate constant (per hour),

t = sample temperature (deg C)

$$\therefore \text{at sample pH}, k_{pH} = k_{pH=2} * 10^{(pH-2)}$$

Potential Contribution of Acid Hydrolysis in GW Samples



In-Situ Acid Hydrolysis?

- Rapid hydrolysis of MTBE to TBA on strongly acidic ion exchange resin (O'Reilly et al. 2001)
  - Measured rate constant: 0.79 d^{-1} at pH=5.5, 25 ^{0}C
  - Postulate a similar mechanism in subsurface, especially in clay geology
  - Expected rate constant in neutral ground water: 0.025 d^{-1} at 25 ^{0}C

Natural Biodegradation of TBA

Summary of Published/Ongoing Research

Aerobic

- Salanitro et al., (2000)
- Bob Borden and others, (Battelle 1999 poster)
- USGS papers (ES&T 2000, 2001)
- John Novak and others, (early 1990s)
- BioGAC is being looked as potential technology for ex-situ treatment
- Ongoing API study

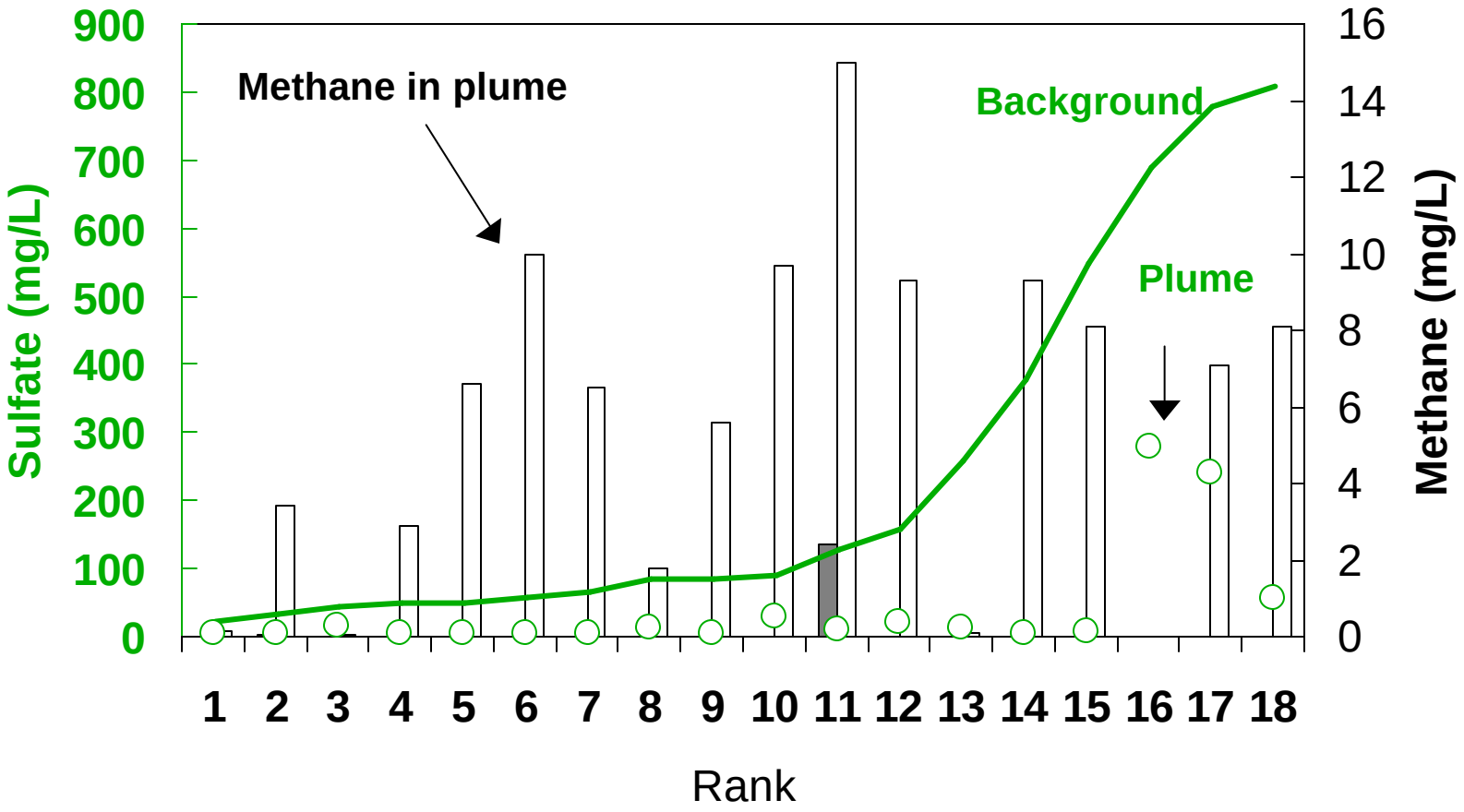
Anaerobic

- Mike Day, 2001 (MNA of TBA in TX)
- BP-EPA field data from 1999-2000 survey
- Kevin Finneran, ES&T 2001 [Fe(III)]
- USGS paper in ES&T 2002 (nitrate, Mn(IV), and sulfate)

API Study on MTBE MNA (initiated in 2000)

- Phase I: Site Selection
  - Selected 18 sites after reviewing ~ 60 sites (BP, Chevron, ExxonMobil)
  - no ongoing remediation, decent characterization and stable/decreasing MTBE plume
  - 13 CA, 4 NJ and 1 PA
- Phase II: Field Monitoring for Geochemical Indicators
  - One time ground water sampling and analytical work by Microseeps
  - Data evaluation complete, 10 sites recommended for follow-up research (Battelle 2001 manuscript)
- Phase III: Laboratory Microcosms with ^{14}C-MTBE and ^{14}C-TBA
  - Surbek-Art Environmental/University of Oklahoma (Dr. Joe Suflita)
  - **Aerobic and Anaerobic incubations**
  - **10 incubations with ^{14}C-MTBE**
  - **4 incubations with ^{14}C-TBA**

Methane and Sulfate in Ground Water – API Study



Similarity of Plume Geochemistry

			BP-EPA 74 Sites	API 18 Sites
Plume Geochemistry		**Designation**	**Number of Sites (% of Sites)**	**Number of Sites (% of Sites)**
Methanogenic (methane > 0.5 mg/L)	Sulfate depleted	M+SD	43 (58%)	8 (44%)
Methanogenic (methane > 0.5 mg/L)	Sulfate available	M+SA	5 (7%)	6 (33%)
Weakly methanogenic (methane < 0.5 mg/L)	Sulfate depleted	WM+SD	8 (11%)	1 (6%)
Weakly methanogenic (methane < 0.5 mg/L)	Sulfate available	WM+SA	5 (7%)	0 (0%)
Nitrate depleted, no methane (nitrate N < 0.05 mg/L)	Sulfate available	ND+SA	13 (17%)	3 (17%)

76% to 83% of all sites are anaerobic (M+SD, M+SA or WM+SD)

API - Ongoing Microcosm Studies

^{14}C-MTBE incubations for all sites

Site ID	Geochemistry	^{14}C-TBA treatment?	Other amendments
Millbrae, CA-1	M+SA	No	Sulfate; two samples
Westlake, CA	M+SA	Yes	
Redding, CA	M+SD	No	
Monessen, PA	M+SD	Yes	Sulfate
San Mateo, CA	M+SD	Yes	
San Jose-2, CA	M+SA	No	
Agoura Hills, CA	ND+SA	Yes	Sulfate; Nitrate
San Jose-1, CA	ND+SA	No	
Petaluma, CA	M+SD	No	Sulfate
Millbrae, CA-2	M+SA	No	Sulfate; two samples

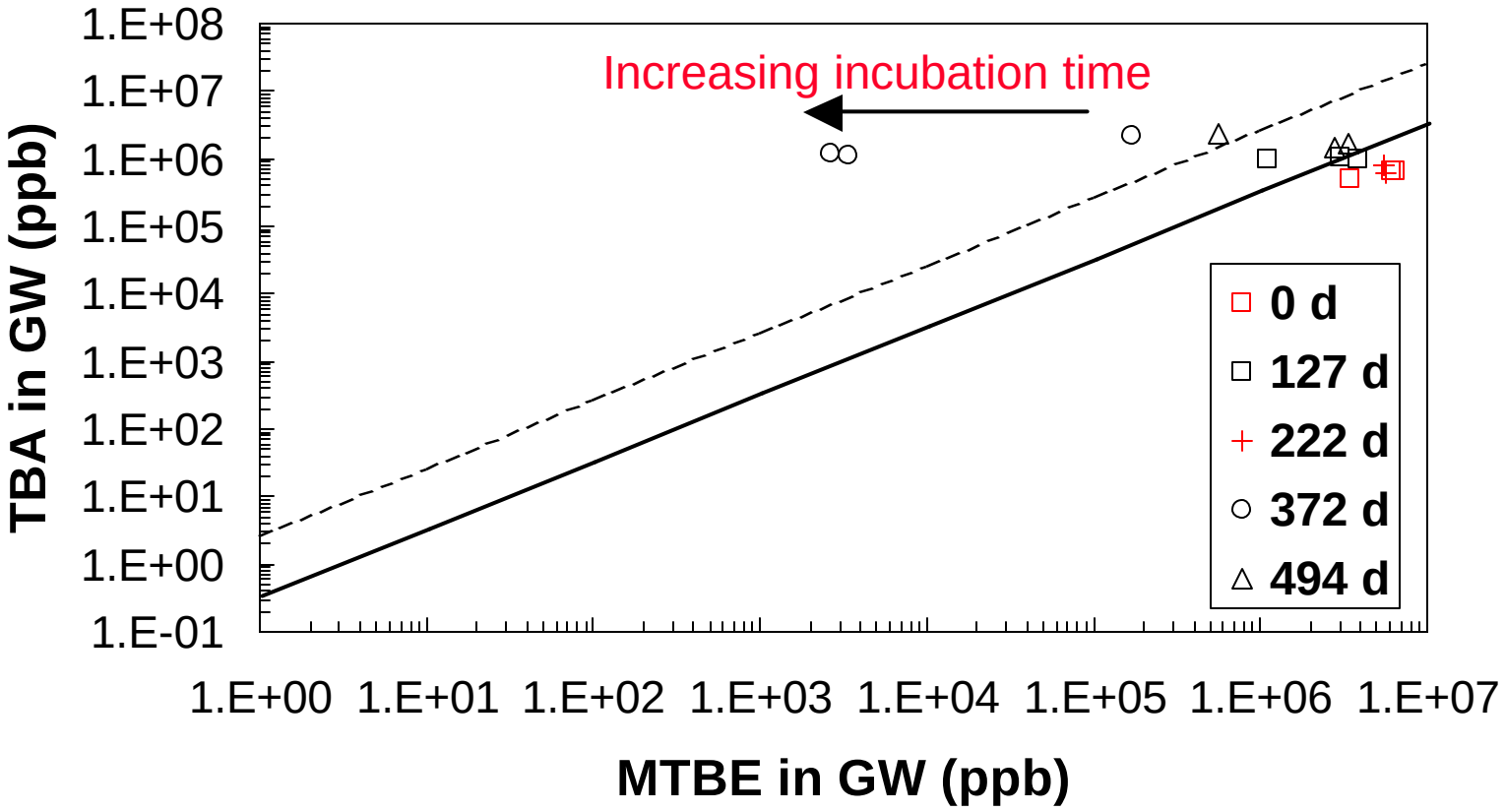
API - Ongoing Microcosm Studies

^{14}C-MTBE incubations for all sites

Site ID	Geochemistry	$^{14}CO_2$ recovery from ^{14}C-TBA aerobic degradation at 200 days?	$^{14}CO_2$ recovery from ^{14}C-MTBE aerobic degradation at 200 days?
Millbrae, CA-1	M+SA	-	72%
Westlake, CA	M+SA	95%	74%
Redding, CA	M+SD	-	92%
Monessen, PA	M+SD	67%	39%
San Mateo, CA	M+SD	45%	79%
San Jose-2, CA	M+SA	-	60%
Agoura Hills, CA	ND+SA	53%	none
San Jose-1, CA	ND+SA	-	none
Petaluma, CA	M+SD	-	none
Millbrae, CA-2	M+SA	-	53%

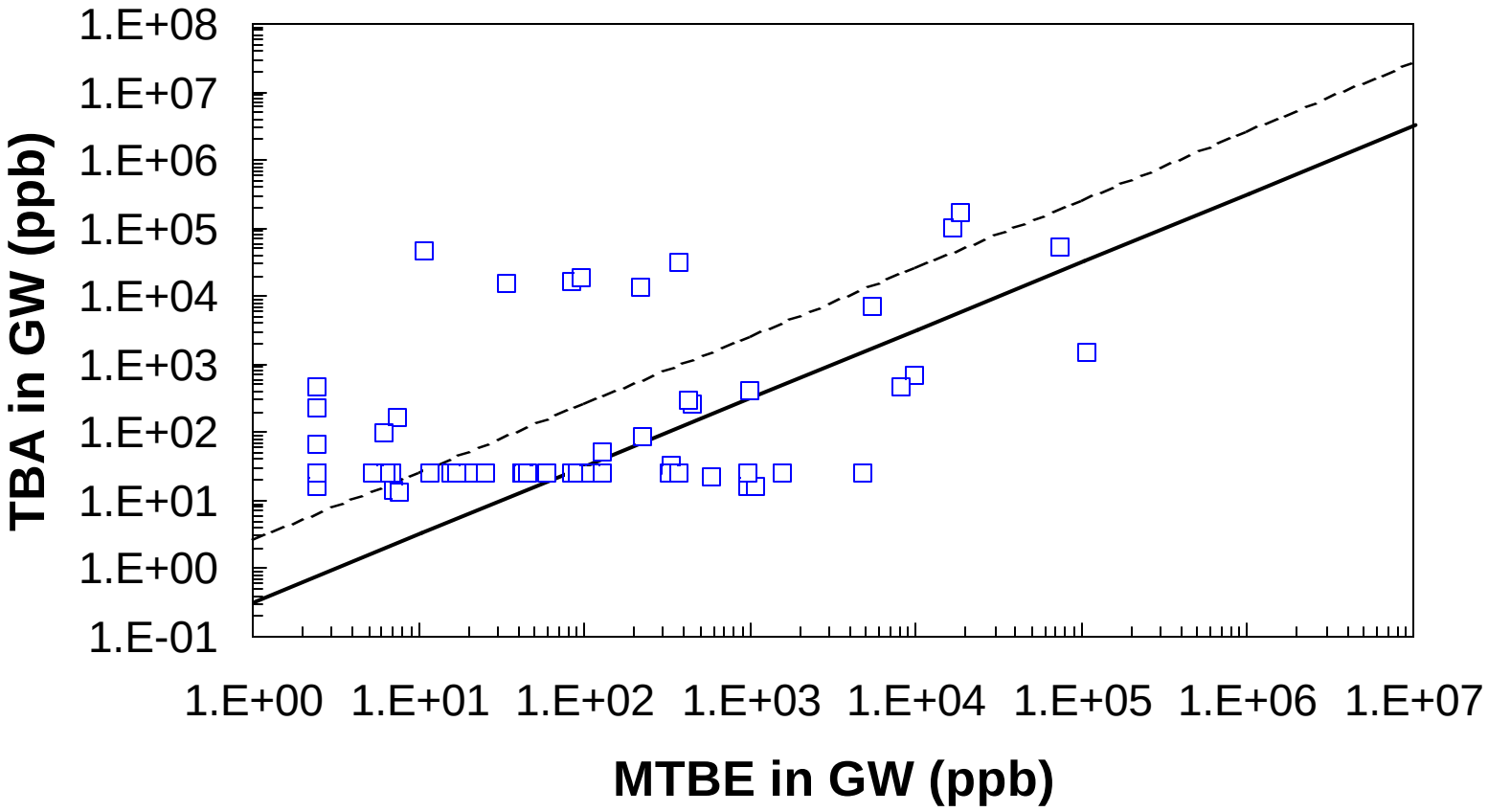
Questions?

TBA in TX Microcosms (anaerobic) EPA Study



Personal communication with Dr. John Wilson, USEPA ORD

TBA in GW – CA Sites in API Study



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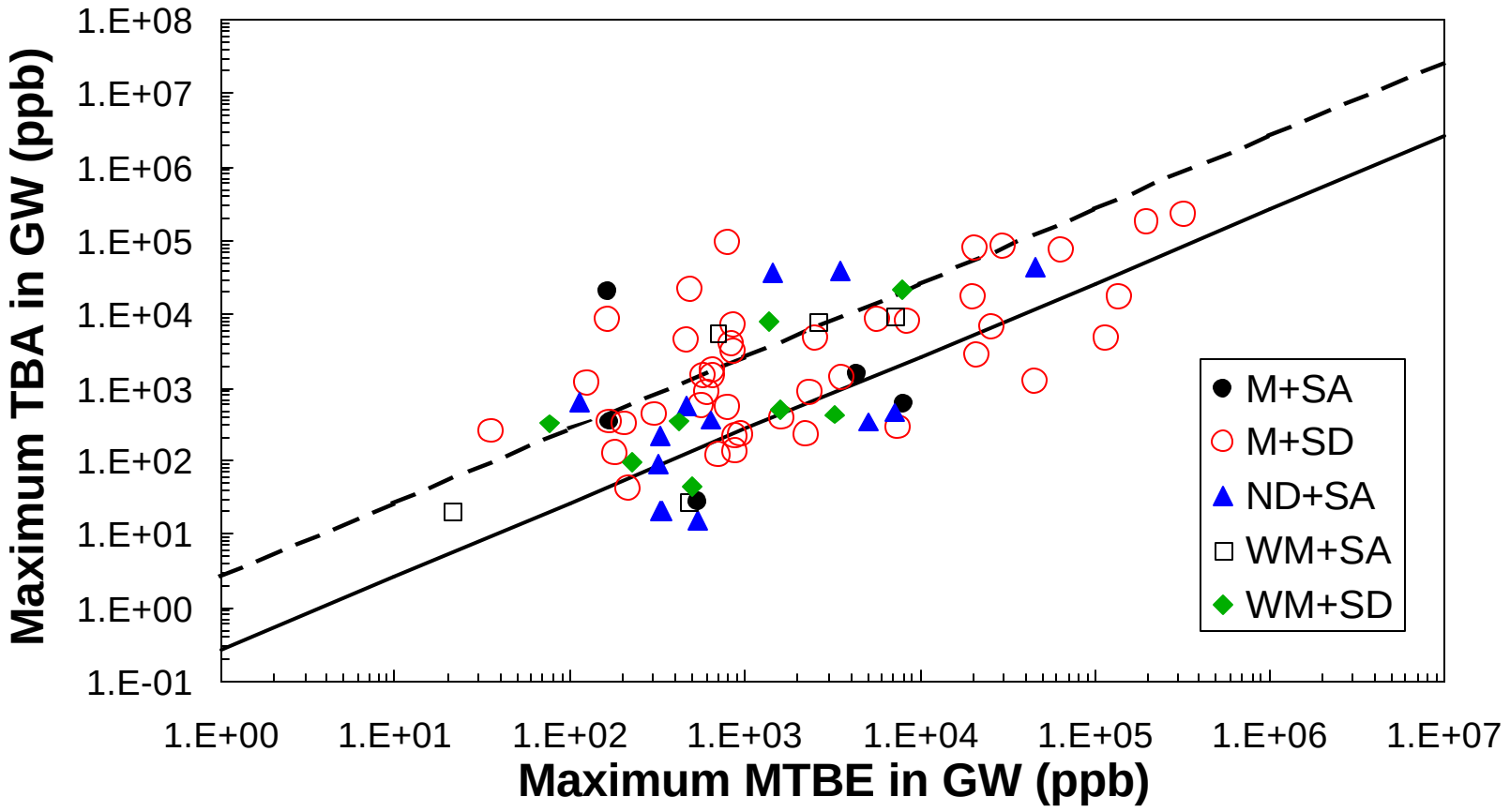

About a third of all sites suggest MTBE biodegradation to TBA

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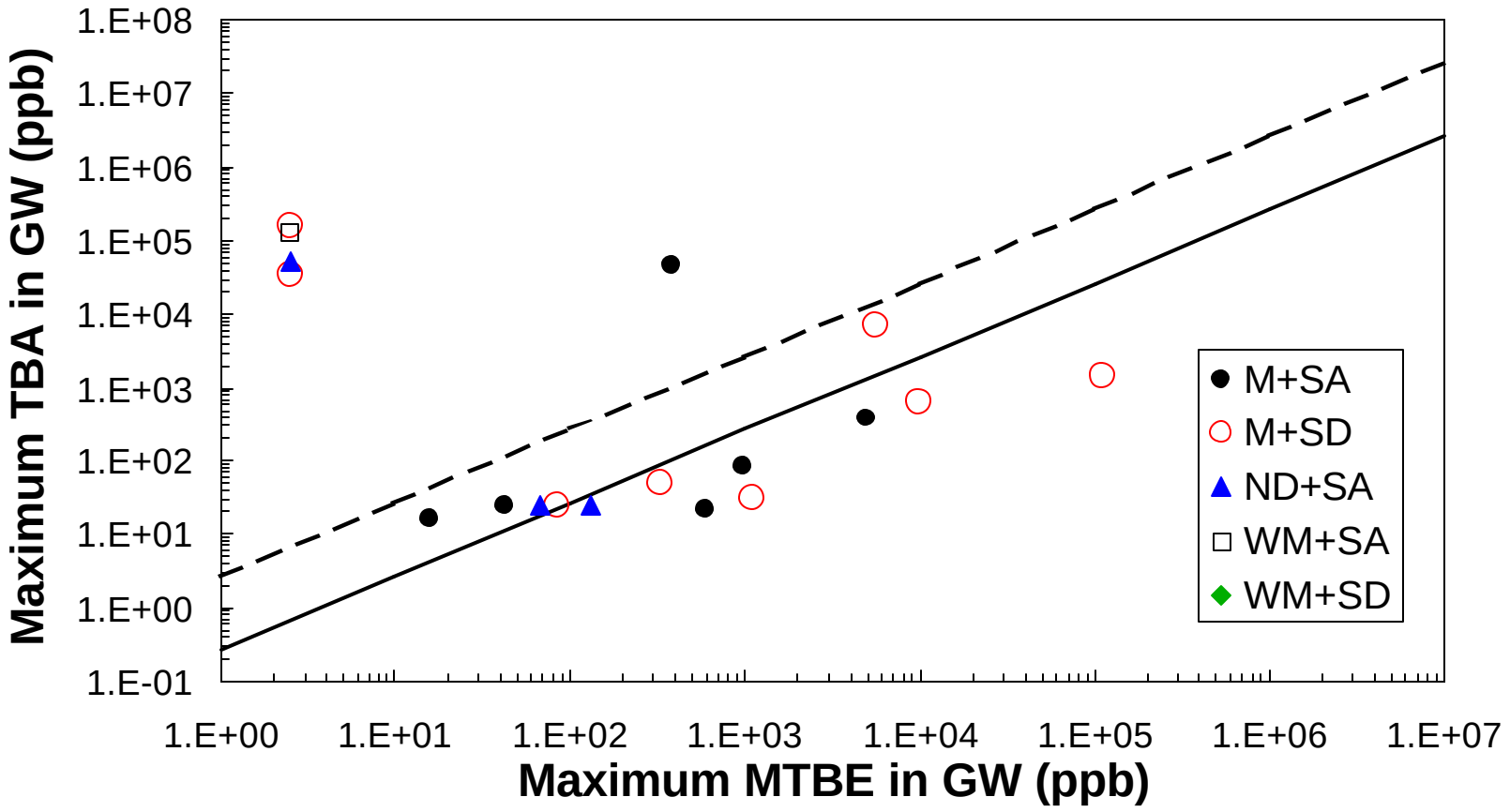
API Study



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